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Effect of Anions on the Sodium Adsorption Capacity and Electrophoretic Mobility of Sodium Saturated Utah Bentonite

Theron G. Sommerfeldt
Utah State University

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EFFECT OF ANIONS ON THE SODIUM ADSORPTION CAPACITY AND ELECTROPHORETIC MOBILITY OF SODIUM SATURATED UTAH BENTONITE

by

Theron G. Sommerfeldt

A dissertation submitted in partial fulfillment
of the requirements for the degree

of

DOCTOR OF PHILOSOPHY

in

Soil Science

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Theron G. Sommerfeldt

INTRODUCTION

Sodium saturated Utah bentonite was equilibrated in several concentrations of various sodium salt solutions. The effect of anions on the amount of sodium adsorbed was determined. The effect of anions on the electrophoretic mobility of the clay was also studied. The results are reported herein.

Anions, are generally considered, in the field of surface chemistry, to have no influence on the amount of cations adsorbed or the electrophoretic mobility of negatively charged colloids (5, 10, 28, 41). There is evidence (2, 7, 24, 26, 27, 33) to indicate that anions sometimes have an appreciable effect. If anions influence the amount of cations adsorbed and the electrophoretic mobility of clay in soil material then they must have an influence on the surface potential. Many of the properties of soils are dependent upon their surface potential. Information concerning the amount of change in surface potential could be of value in determining what effect irrigation water would have on the soil. This knowledge would also be of value in reclaiming sodic soils.

Current methods (39, 40) for determining the suitability of water for irrigation do not involve direct effects of anions on the surface properties of soil materials. If the surface properties of negatively charged soil materials are sufficiently influenced by their anion environment, such that these properties are changed by appreciable amounts, then methods for determining suitability of water for irrigation should give consideration to the effects of anions.

The hydraulic conductivity of soil materials often becomes very small during the reclamation of alkali soils because of the dispersion of the colloids. This is a serious problem as the rate of reclamation is dependent upon the rates of leaching and drainage which in turn depend upon the hydraulic conductivity. Hence, conditions which reduce the tendency of the soil materials to disperse should be employed. The tendency of a soil to disperse is a function of the surface potential; the greater the surface potential the greater the tendency. Therefore, if the surface potential of a soil material can be effectively reduced through its anion environment then the problem of preventing dispersion should be reduced accordingly.

Also, by reducing the potential of the surface, the degree of sodium saturation should be reduced. Sodium is the most readily replaced cation of those commonly found in alkali soils (43). Hence, if the surface potential of the material was decreased, sodium should be more readily desorbed than the other cations. This would result in a reduction in degree of sodium saturation of the soil material.

LITERATURE REVIEW

The amount of sodium adsorbed by soil colloids in the presence of sodium salts has been shown to vary with the anion present. Binder-Barkava and Ravikovitch (3) reported greater sodium adsorption by soil colloids when they were in the presence of sodium sulfate, than when in the presence of either sodium chloride or nitrate. Similarly, Kelley (23) reported more sodium saturation when the soil was in the presence of sodium carbonate than when in the presence of either sodium chloride or nitrate. Yolo soil was treated with 10 milliequivalents of either sodium chloride, sodium nitrate or sodium carbonate. The soil was found to have adsorbed 2.3, 2.9 and 5.0 milliequivalents of sodium when in the presence of the chloride, nitrate and carbonate ions respectively. The amounts of calcium and magnesium in the equilibrate were less when the anions were carbonate than when they were chloride or nitrate. Not only was there more sodium adsorbed but more cations were retained by the carbonate system. No mention was made of the amount of soil treated or the pH of the systems. In the presence of the carbonate ion, Kelley (23) reasoned that calcium and magnesium had been precipitated, leaving only sodium to saturate the soil colloid. This reasoning is supported by Christensen and Lyerly (8).

Wilcox, Blair and Bower (42) reported significant anion effects on the exchangeable sodium percentage of Hanford sandy loam when the solution concentration was 5 milliequivalents per liter or more and the soluble sodium percentage was 75. The amount of sodium saturation was less when the anion was chloride than when it was bicarbonate. They explained these results as a consequence of the precipitation of calcium as carbonates, and conclude that waters having more than 2.5 milliequivalents per liter of residual sodium carbonate are not suitable for irrigation.

In studies determining the effects of irrigation waters on soils, it was found that anions in the system affected the degree of sodium saturation. Lewis and Juve (26) reported that high concentrations of carbonate and bicarbonate ions upset equilibrium relations of the cations, resulting in poor correlation between the exchangeable sodium percentage of the soil and the sodium adsorption ratio of the water. This was attributed to precipitation of calcium and magnesium. Longenecker and Lyerly (27) reported no correlation between the salt composition of irrigation waters and the sodium status of the field soils. This was attributed to a lack of equilibrium between the soils and waters, and the high gypsum content of the soils. Fine and co-workers (11) reported that where gypsum was present the degree of sodium saturation was less than where it was not present. Babcock and co-workers (2) worked with synthetic waters having a total salt concentration of 10 milliequivalents per liter. They varied the $Na^+:Ca^{++}$ and $Cl^-:HCO_3^-$ ratios and observed that the quantity of bases adsorbed increased when the anion was bicarbonate. They attributed this excess base saturation to the formation of mono-hydroxy calcium and magnesium ions.

Eaton (10) reported that if the concentration of soluble calcium and magnesium exceeded that of the carbonate and bicarbonate ions in solution there would be little danger of the soil becoming sodium saturated. However, the probability of sodium saturation would increase with evaporation and plant uptake of the soil water. This would result in an increase in concentration of the soil solution causing the precipitation of calcium and magnesium and favoring sodium saturation of the soil complex.

Babcock and others (2), in a study of irrigation water on soil properties thought that calcium and magnesium were not precipitated as insoluble carbonates but formed mono-hydroxy ions, that is, $CaOH^+$ and $MgOH^+$, as proposed by Bower and Truog (7). These ions are adsorbed on the soil in this form. This would increase the amount of cations adsorbed by the soil. Thus it appears, that if sodium was the intermicellar cation in greatest abundance that an increase in the degree of sodium saturation should be the result.

Kelley, Brown and Liebig (25) reported that essentially equal amounts of sodium were adsorbed by soil held at constant pH. This was true when the anion was either chloride or bicarbonate. They observed that sodium adsorption varied directly with pH. On the other hand, the U. S. Salinity Laboratory Staff (40) reported more sodium adsorption on a soil in the presence of bicarbonate than in the presence of chloride ions. Apparently the pH in this latter study was not held constant.

The concentration of a given cation required to bring about flocculation of negatively charged colloids has been shown to vary with the anion present. Oakley (32), and Joseph and Oakley (22) reported that hydroxides of sodium and calcium were less effective in causing flocculation of clay than were the corresponding chlorides. Ramdas and Mallik (34) reported that soils leached with 1 percent sodium carbonate solution dispersed, whereas, soils leached with 5 percent sodium chloride solution were not. The permeability of the dispersed soil was restored when the 1 percent sodium carbonate solution was replaced with a 5 percent sodium chloride solution, but not when replaced with water. They concluded that sodium carbonate reduced the permeability of the soil more than sodium chloride and that sodium chloride may have a place in reclamation procedure for saline alkali soils.

Overbeek (33) has shown that the concentration of cations necessary to cause flocculation of a negatively charged arsenic sulfide varied with the anion present. A concentration of 49.5 milliequivalents per liter of potassium chloride was required to cause flocculation as compared to a concentration of 65.5 milliequivalents per liter of potassium sulfate. A concentration of 1.44 milliequivalents per liter of magnesium chloride was required for flocculation as compared to 1.62 milliequivalents per liter of magnesium sulfate. He (33) also reported that highly charged ions having the same charge as the colloid often lead to higher flocculation values which has been referred to as the "relieving effect." However, when the flocculation values are studied in terms of ionic activity rather than concentration, these effects disappeared.

Hydrogen and hydroxyl ions are surface potential determining ions on certain surfaces (12, 33). The negative potential of pyrex glass has been shown by Overbeek (33) to increase when placed in the presence of potassium hydroxide. When in the presence of a 1 micromole per liter solution of potassium hydroxide, the zeta potential of the glass was about 182 millivolts. As the concentration increased, the zeta potential increased to a maximum of about 184 millivolts at a concentration of about 5 micromoles per liter. Then it decreased as the concentration increased. When the solution was potassium nitrate and at a concentration of 1 micromole per liter, the zeta potential of the pyrex was about 166 millivolts and increased concentrations of potassium nitrate lowered the potential of the pyrex. Throughout the concentration range of 1 micromole per liter to 10 millimoles per liter of these two salts, the zeta potential of the pyrex was at least 15 millivolts greater in the presence of potassium hydroxide than in the presence of potassium nitrate at the same concentrations.

Kelley (24) gave evidence that the surface potential of soils varies with pH. He reported that the amount of metallic cations adsorbed by the soil increased as the pH increased. Schofield (35) reported additional negative charges developed on illite type clay with an increase in pH above six.

Even though there is evidence that the anion can affect the surface properties of soil materials, this phenomenon has received little attention. Bolt and Miller (5) considered the effect of the anion in a soil system to be negligible. The influence of anions on the flocculation values of solutions for negatively charged colloids was considered by Verwey and Overbeek (41) as being subordinate. Eaton (10) states: "So far as is known, the anions are without influence on the base equilibrium between solution and clay." Marshall (28) recognizes Mattson as one of the few investigators who has been concerned with the effect of the ion having the same charge as the colloidal particle.

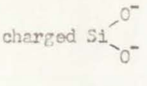
Mattson (29) has studied the effects of anions on negatively charged soil materials. He studied their effects as well as those of cations on such properties as the potential of the colloid, swelling and distribution of the different ions throughout the system. He applied the Donnan theory and Nernst formula to explain the phenomena of the ion distribution and potential differences. By application of the Donnan equation, $x^2 = y(y-z)$, where x is the molar concentration of the anion and cation, for a uni-univalent type salt in the solution, y is the molar concentration of the same ions in the micellar atmosphere and z is the cation saturation on the colloid, he arrived at the ion distribution. By combining this with the Nernst formula he arrived at a potential difference (P.D.) of the colloid;

$$\text{P.D.} = (RT/F)\ \ln(x/y) = 58 \log (x/y)$$

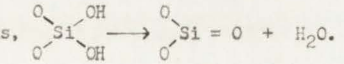
where R, T and F are the gas constant, absolute temperature and Faraday constant respectively. This was extended to include systems containing salts other than uni-univalent type.

His (29) results showed that, when the same concentration of salts was used, the potential difference was the same for the sulfate as it was for the chloride and ferrocyanide. However, the amount of sodium adsorbed by the colloid was greater in the presence of sulfate than chloride. He attributed this difference to valence and osmotic pressure.

The charge density, degree of polymerization and solubility of silica, has been reported as being affected by its environment. Bolt (4) reported the charge density of silica increased with the electrolyte concentration as well as with pH. In a study of the depolymerization of silica in sodium hydroxide, Greenberg (15) reported only

SiO^- and SiOH groups occured below pH 11.8. Above this pH doubly charged  $\mathrm{Si}{<}^{O^-}_{O^-}$ groups may occur. Sears (37), working in the pH range of 9.0 to 11.5, found the number of SiO^- and SiOH groups increased with pH. At pH 9.0 there were about 1.26 and at pH 11.5 there were about 3.7 ionized groups per square millimicron. This latter value is in agreement with Heston, Iler and Sears (20), who, working in the pH range of 10.5 to 12.0, reported the number of hydroxide ions adsorbed by the silica to be 3.5 ± 0.3 per square millimicron. However, working with soils, Bower, Reitemeier and Fireman (6) observed that, within the pH range of 7.0 to 11.0 the hydroxide ions had very little effect on the charge density of soils not containing kaolinitic materials. Where kaolinitic materials were present the charge density, as indicated by cation exchange capacity, increased appreciably from pH 9.0 to pH 10.0. This was explained by the presence of many weakly acidic groups on kaolinitic materials.

The degree of polymerization of silica appears to be a function of the number of hydrogen bonds, pH and anions present. In a study of surface functionality of amorphous silica using infrared spectroscopy, McDonald (30) suggested the surface sites are geometrically located such that surface groups are kept from reacting with each other, although they may link together by formation of hydrogen bonds. This linking would only occur where crystalline forms are absent or where defects in the crystal appear. Defects such as cracks, impurity atoms, dislocation and intersections of crystallites, which are rather common in the disordered structure of amorphous silica, may cause linking. Greenberg (15) reported that the degree of depolymerization of silica increased with pH. Also when sulfate ions were added to the system the degree of depolymerization was depressed. In another study, Greenberg and Price (16) observed that the solubility of silica in sodium hydroxide, pH 10.15, was 4.75 millimoles per liter. When sodium sulfate was added to the system, at the rate of 0.08 equivalents per liter, the pH dropped to 9.50 and the solubility of the silica dropped to 2.75 millimoles per liter. It appears from their data that this difference in solubility of silica is not wholly the result of the sulfate ion alone, but can be partially attributed to the change in pH as this was in the range where the solubility was affected by pH. Changes in pH between 7.0 and 9.0 did not affect the solubility of silica but above 9.0 the solubility increased with pH.

Greaves and Linnett (14) reported that there are about eight OH groups per millimicron of silica. Sears (37) also reported eight OH groups per square millimicron of silica, of which about four ionize. But at room temperature some of the OH groups may be lost through dehydration to form an oxygen bridge, resulting in a distortion of the surface, that is, 

Schofield and Samson (36) reported the charge density of kaolinite clay varied with pH. They suggested the same would be true with all the clays. At very high pH's, the silicate sheets carry negative charges as a result of loss of hydrogen from the hydroxides. Also, the alumina adsorbs and desorbs hydrogen, depending upon pH. This latter occurs at lower pH's than that in the silicate layer.

The solubility of montmorillonite clay, as reported by Nutting (31), varied with concentration of sodium carbonate. The amount of silicon in solution increased with concentration to 0.02 normal, then it was depressed slightly at 0.05 normal and then increased with concentration of the sodium carbonate to 0.1 normal.

It is evident that the effect of environmental factors on surface properties of negatively charged silica materials can be very important and that many of the anomalous effects may be attributed to the neglected anions in the system. Težak and others (40) consider present theories related to colloidal stability too speculative. They consider three regions in a colloidal system: the core, the diffuse double layer and the intermicellar solution, and that the characteristics of the diffuse double layer may be the results of specific interactions of the constituents in both the surface and liquid phases.

The Debye-Hückel theory for solutions has been applied to colloidal systems by Verwey and Overbeek (43), Derjaguin (9), Audubert (1) and others. In general there is a lack of agreement between theoretical and experimental results. However, Audubert (1) reported that the application of the Debye-Hückle theory to colloidal systems allows conclusions to be drawn about the processes by which the particles become charged. Also it allows the estimation of the surface electrochemical phenomena, as compared with selective adsorption and chemical reactions which may occur at the surface.

In conclusion, it is evident from the review of literature, that the surface properties of many negatively charged silicate materials can be greatly influenced by the anion present. Hydroxides and anions of weak acids tend to increase the degree of sodium saturation, cation exchange capacity, flocculation values and surface potential, whereas the anions of strong acids tend to lower these values. Current solution theory does not give reason for the results, however, valuable information may be derived from its use. Further research, studying the effects of anions on surface properties of the silicate materials can be advantageously done in order to more fully understand the reactions and interactions involved in such systems.

MATERIALS AND METHODS

Utah bentonite was sodium saturated and used as stock material. To sodium saturate the clay, raw material was washed with 0.1 normal hydrochloric acid to remove carbonates. The clay was thoroughly shaken with hydrochloric acid. It was then allowed to settle out of suspension, the supernatent solution was decanted off, fresh acid solution was added, and the process of shaking, settling and decanting repeated. This was done until there was no evidence of effervescence to acid. At completion the pH was 3.0.

The carbonate free clay was then sodium saturated by washing in a solution of one normal sodium chloride until there was no trace of carbonate in the effluent. The chloride ions were then removed from the system by washing the clay with dilute solutions of sodium hydroxide until there was no trace of chloride in the system, as indicated by the sodium nitrate test. During this process, the pH of the system rose to 10.4. Distilled water was then used to wash out the excess sodium hydroxide and lower the pH. After about 20 washings, the pH was lowered to 9.3 and remained steady at this point. To further reduce the pH, ethanol (95 percent) was used to wash the clay. After seven washings with ethanol the pH remained steady at 8.0. The clay was then brought into suspension in water and transferred to pans and dried. The air dried clay was crushed to pass a 20 mesh sieve. This clay was used as stock material for this study. The pH of the saturation paste was 8.1 and the amount of cations adsorbed was 93 milliequivalents per 100 grams of clay material.

Samples of the stock material were equilibrated in different concentrations of sodium chloride, bromide, iodide, sulfate, bicarbonate and hydroxide. The concentrations, expressed in ionic strength[1], were: 0.01, 0.1, 0.5 and 1.0.

Effects of the initial pH of the equilibrating solutions were studied by equilibrating the clay in the sodium halide and sulfate solutions at pH levels 7.2 and 10.5. At 7.2 the solutions were unadjusted. Sodium hydroxide was used to raise the pH to 10.5.

To equilibrate the clay, samples of 2 grams each were placed in weighed centrifuge tubes, then 32 milliliters of the equilibrating solution was added. The tubes were then capped and shaken for one hour, after which the clay was separated from the solution by centrifuge and decantation. The decanted material was saved for analysis.

In preliminary studies, it was found that the amount of cations adsorbed by the material equilibrated for 10 minutes was the same as that for one hour. Hence it was assumed one hour was sufficient time for equilibration in this study.

After decantation, the centrifuge tubes were reweighed with the clay, to determine the amount of solution retained. From the amount of solution retained and its concentration, from equilibrate analysis, the amount of soluble salts was then determined.

The ammonium acetate extractable cations were obtained by the method outlined by the U. S. Salinity Laboratory Staff (40).

The pH, before and after equilibration, was determined with a

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[1] Ionic strength μ is: $\mu = \frac{1}{2}\Sigma CZ^2$ where C is molar concentration and Z is the valence of the ion.

Beckman Zeromatic pH meter using standard glass electrodes.

Changes in cation and anion concentrations in the equilibration extract were determined. Sodium and potassium were determined with a Perkin-Elmer flame photometer. Calcium and magnesium were determined by Versenate methods. Iron and alumina were determined by precipitation with ammonium hydroxide. Halides were determined by conductometric titration. Sulfates were determined gravimetrically. Bicarbonates and hydroxide were determined by volumetric titration, using sulfuric acid. Soluble silicon was determined by the silico-molybdate method outlined by Jackson (21).

The exchangeable cations and soluble silicon in the ammonium acetate extract were determined by the same methods used in the equilibration extract analysis.

The electrophoretic mobilities of the clay, suspended in the equilibration extract, were determined by the moving boundary method, using a U tube apparatus, fabricated in the laboratory for this purpose. Platinum electrodes were used and the source of power was a Heathkit variable voltage unit, Model PS-3, supplied by the Heath Company, Benton Harbor, Michigan.

RESULTS

The amount of sodium adsorbed by Utah bentonite was found to vary with the kind of anions and ionic strength of the solutions in the system, as shown in Figure 1. The differences were magnified by increased ionic strength (concentration) of the solutions. At an ionic strength of 1.0 the amount of sodium adsorbed was: 66, 68, 76, 77, 94 and 115 milliequivalents per 100 grams of clay when the anions were bromide, iodide, chloride, sulfate, bicarbonate and hydroxide respectively.

The electrophoretic mobility of the clay was also affected by the anions in the system, as shown in Table 1. However the data are so few that only general results can be observed. Comparing the data of Table 1 with those of Figure 1, it appears that under conditions where the amount of sodium adsorbed was the greatest the electrophoretic mobility was largest. As the amount of sodium adsorbed decreased the electrophoretic mobility also decreased, except for the iodide and bromide at ionic strength of 0.01. At the higher salt concentrations, the suspensions were unstable and the clay settled out, hence the electrophoretic mobility could not be measured.

Analysis of the equilibration and ammonium acetate extracts of the clay material gave no indication of either soluble or exchangeable calcium, magnesium, potassium, iron or aluminum being present. Hence, it appears that the differences observed in the amount of sodium adsorbed and electrophoretic mobilities are not the results of confounded

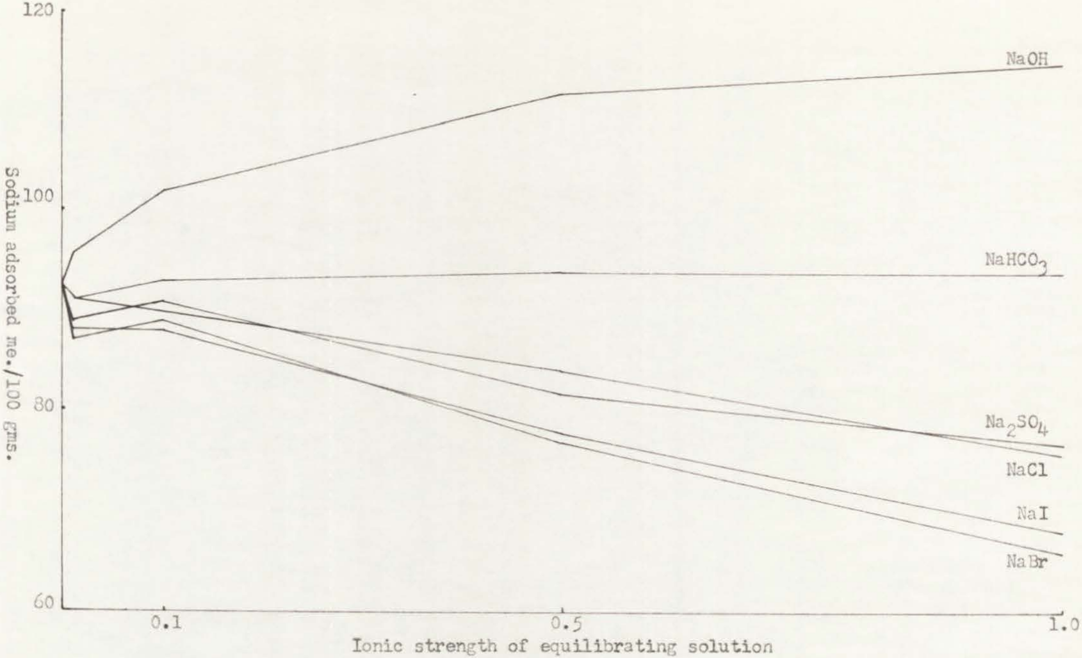

Figure 1. Effect of ionic strength and anions of the equilibrating solution on the amount of sodium adsorbed by Utah bentonite

Table 1. Effect of ionic strength and anions of the equilibrating solution on the electrophoretic mobility of sodium saturated Utah bentonite

Ionic strength of solution	Electrophoretic mobility in microns per second					
	NaCl	NaBr	NaI	Na_2SO_4	$NaHCO_3$	NaOH
0.01	6.67	5.00	4.17	6.46	6.67	9.17
0.10	3.33	1.67	-	2.92	3.33	8.34
0.50	-	-	-	-	-	-
1.00	-	-	-	-	-	-

reactions with the anions and calcium and magnesium, as has been proposed (2, 7, 8, 23), nor with iron and aluminum. The pH of the ammonium acetate extract indicates hydrogen ions were not adsorbed on the clay in significant amounts. When the anions were halides and sulfate and at the lower concentrations of sodium bicarbonate and hydroxide, the pH of the extract was very nearly the same after extraction as it was initially, as shown in Table 2. At higher concentrations of sodium bicarbonate and hydroxide, the pH of the extracting solution increased, as would be expected.

Table 2. The pH of ammonium acetate extract (pH of original was 6.9.)

Ionic strength	NaCl	NaBr	NaI	Na_2SO_4	$NaHCO_3$	NaOH
0.01	6.90	6.85	6.88	6.90	6.90	6.90
0.10	6.98	6.88	6.88	6.90	6.95	7.25
0.50	6.90	6.88	6.90	6.90	7.35	7.72
1.00	6.92	6.90	6.90	6.90	7.30	8.00

For the solutions studied, namely the halides and sulfate, the initial pH of the equilibration solution had no significant effect on the amount of sodium adsorbed or on the electrophoretic mobility of the clay, as shown in Table 3.

Table 3. Effect of pH on amount of sodium adsorbed and electrophoretic mobility of sodium saturated Utah bentonite when equilibrated in various sodium salt solutions

pH of original solution	Ionic strength	Amount of sodium adsorbed me./100 gms.				Electrophoretic mobility in microns/sec.			
		NaCl	NaBr	NaI	Na_2SO_4	NaCl	NaBr	NaI	Na_2SO_4
7.2	0.01	91	87	87	89	6.67	5.00	4.17	6.25
	0.10	91	88	88	90	3.33	1.67	-	2.50
	0.50	83	77	79	81	-	-	-	-
	1.00	76	66	63	76	-	-	-	-
10.5	0.01	91	87	88	89	6.67	5.00	4.17	6.67
	0.10	90	90	87	92	3.33	1.67	-	3.33
	0.50	84	77	77	82	-	-	-	-
	1.00	75	66	68	78	-	-	-	-

It is of interest to note that the final pH of the equilibration extract was, in most cases, different from that of the original, as shown in Table 4. The pH of the equilibration extract from solutions having an original pH near seven was greater than that of the original, in all cases excepting for the chloride systems. When the pH of the original solution was 10.5, the pH of the equilibration extract was less than that of the original. Also, when the anions were bicarbonate and hydroxide, the pH of the solutions were not greatly affected by equilibration.

Table 4. The pH of equilibrating solution before and after equilibration with sodium saturated Utah bentonite

Solution	Time of determination	Ionic strength of solution			
		0.01	0.10	0.50	1.00
NaCl	before	7.3	7.2	7.2	7.2
	after	7.3	7.2	7.1	7.1
	before	10.5	10.5	10.5	10.5
	after	9.4	9.0	8.6	8.6
NaBr	before	7.2	7.2	7.5	7.3
	after	9.2	8.4	7.8	7.4
	before	10.5	10.5	10.5	10.5
	after	9.5	8.8	8.3	8.2
NaI	before	7.2	7.2	7.5	7.9
	after	8.5	7.9	7.4	7.5
	before	10.5	10.5	10.5	10.5
	after	9.4	8.1	8.3	8.4
Na_2SO_4	before	7.5	7.6	7.3	7.3
	after	9.2	8.5	7.5	7.6
	before	10.5	10.5	10.5	10.5
	after	9.5	9.0	8.5	8.4
$NaHCO_3$	before	8.9	8.5	8.3	8.2
	after	9.1	8.5	8.3	8.2
NaOH	before	11.4	12.3	12.4	12.3
	after	11.0	12.2	12.4	12.2

The trends in the sodium ion concentration, as shown in Table 5, follow an inverse relation to the amount of sodium adsorbed, as one would expect, that is, as the amount of sodium adsorbed decreased, the sodium ion concentration in the equilibration extract increased and vice versa.

Table 5. Sodium ion concentration in the various sodium salt solutions following equilibration with sodium saturated Utah bentonite

Ionic strength	Sodium ion concentration me./l					
	NaCl	NaBr	NaI	Na_2SO_4	$NaHCO_3$	NaOH
0.01	2	8	-4	-5	1	0
0.10	0	-4	5	1	-1	-10
0.50	8	5	15	-2	4	-11
1.00	5	24	6	10	26	0

There seemed to be no change in the quantities of anions in solution, except for the bicarbonate and hydroxide ions, as shown in Table 6. The differences observed are considered within the limits of experimental error. This suggests that anion adsorption was not significant, except in the hydroxide and bicarbonate systems. There is a trend indicating hydroxide ion removal with increased ionic strength of the sodium hydroxide, as one would expect from the literature. Also, in the bicarbonate system there was an increase in bicarbonate ions with increased ionic strength. In this system pressure developed during the equilibration process. This would indicate something entered into the gaseous phase, possibly carbon dioxide. This could have affected the results.

Table 6. The anion concentration of the various sodium salts in solution following equilibration with sodium saturated bentonite

Ionic strength	Anion concentration me./1					
	NaCl	NaBr	NaI	Na_2SO_4	$NaHCO_3$	NaOH
0.01	0	0	0	6	3	-2
0.10	1	-4	-4	4	3	-9
0.50	2	-4	15	-4	6	-15
1.00	-5	15	15	1	18	-2

The concentration of soluble silicon in the equilibration extract significantly (r = 0.777) increased with the amount of sodium adsorbed, as shown in Table 7.

Table 7. Soluble silicon in equilibration extract following equilibrating sodium saturated Utah bentonite with various sodium salt solutions

Ionic strength	Soluble silicon me./1					
	NaCl	NaBr	NaI	Na_2SO_4	$NaHCO_3$	NaOH
0.01	82	65	65	75	118	369
0.10	55	49	55	52	65	988
0.50	50	47	50	49	65	1500
1.00	48	44	55	50	65	1662

In the ammonium acetate extract the concentration of soluble silicon was the same from the halide and sulfate systems as well as the same for all ionic strengths within these systems, as shown in

Table 8. In the hydroxide and bicarbonate systems, the concentration of soluble silicon in the extract was 6 and 2 milliequivalents per liter, respectively, less than that of the halides and sulfate.

Table 8. Soluble silicon in ammonium acetate extract from sodium saturated Utah bentonite following various equilibration processes

Ionic strength	Silicon in ammonium acetate extract me./1					
	NaCl	NaBr	NaI	Na_2SO_4	$NaHCO_3$	NaOH
0.01	40	40	40	40	38	34
0.10	40	40	40	40	38	34
0.50	40	40	40	40	38	34
1.00	40	40	40	40	38	34

The high concentration of soluble silicon in the equilibration extract from the hydroxide systems, to a lesser degree in the bicarbonate, as shown in Table 7, suggests the clay underwent degeneration during the equilibration process. The nature of this degeneration was such that the concentration of soluble silicon during the extraction process was more limited than in the halide and sulfate systems, as shown in Table 8.

Absence of alumina in either the equilibration or ammonium acetate extracts indicates it had either been precipitated, probably as a basic salt, or it was not released from the clay crystal.

DISCUSSION

Based on the results, as presented, the anion environment had an effect on the amount of sodium adsorbed by the clay (Figure 1, page 17). The amount of sodium adsorbed varied with the kind of anions and ionic strength of the solutions in the systems. In general, the effect of a specific anion was magnified with increased ionic strength.

The data have been summarized and analysed from different approaches to determine if the anions had a direct effect on the amount of sodium adsorbed or if it was a secondary effect operating through some other factor.

First, the amount of sodium adsorbed by the clay in the various systems was compared at equal activities for all the solutions but that of the bicarbonate. The activities were calculated from mean activity coefficients of the various salts, as given by Glasstone (13) and Harned and Owen (18), for the concentrations used in the equilibrating solutions. The amount of adsorbed sodium per 100 grams of clay was plotted against sodium ion activities, as shown in Figure 2. The effects are different for the several kinds and activities of anions in the systems. The halides in solution influenced the amount of sodium adsorbed in a similar manner as the ionic strength for the same solution, as seen by comparing Figure 1 with Figure 2. In the sulfate system the amount of sodium adsorbed was decreased more than that of the halides with increased sodium activity, but was less with ionic strength.

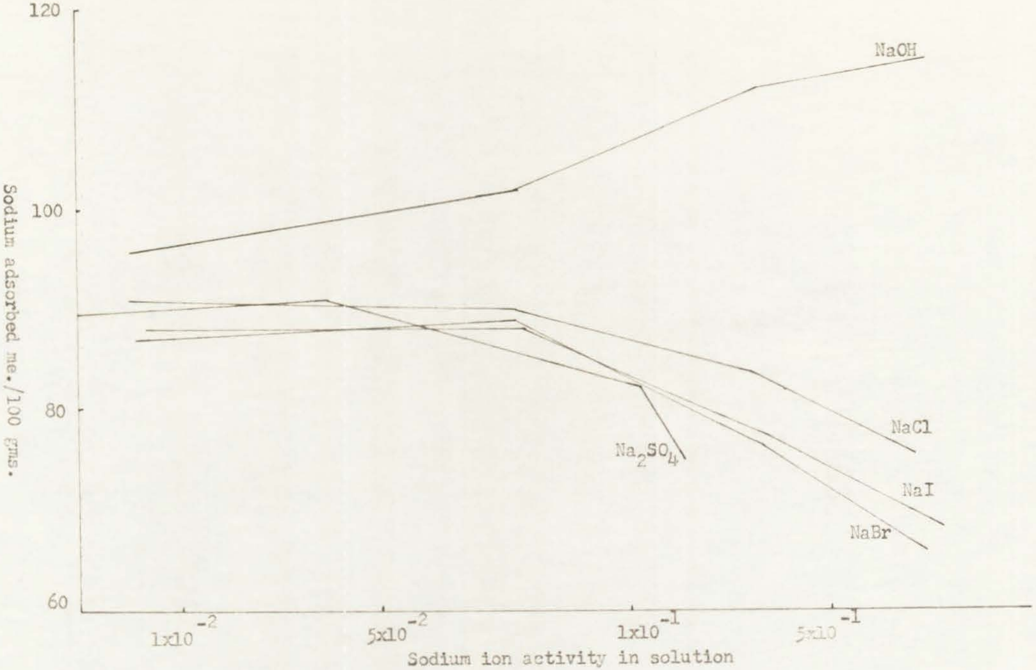

Figure 2. Amount of sodium adsorbed by Utah bentonite when equilibrated in solutions of various sodium ion activities

Second, the amount of adsorbed sodium, without reference to specific anions, was plotted against pH, Figure 3. From this plot, one can see a crude relation between pH and the amount of sodium adsorbed. Generally, the amount of sodium adsorbed increased with pH. The scatter of the experimental points was associated with the different anions, as shown in Figure 4. The general trend was for a positive relation, that is, the amount of cations adsorbed increased with pH. This trend was reversed for the bicarbonates. It is therefore apparent that pH was not solely responsible for the results, since, the anions had different individual effects.

When the clay was equilibrated in the halide and sulfate solutions, the initial pH had no effect on the amount of sodium adsorbed. The amount of sodium adsorbed by the clay was essentially the same when equilibrated with solutions at an initial pH of 10.5 as with those at 7.2, as shown in Table 3, page 19. However the amount adsorbed was influenced by the final pH as already pointed out.

The anion environment also influenced the stability of the clay, as indicated by the amount of soluble silicon found in the equilibration extract (Table 7, page 22). In general, when the clay was equilibrated in solutions containing anions of strong acids it was more stable than when the anions were bicarbonate and hydroxide. From this, one would suspect pH had an effect on the amount of silicon in solution. This possibility was investigated by comparing the amount of soluble silicon with pH, without reference to specific anions, as shown in Figure 5. Only the data from the low pH systems of the halides and sulfate were used. From Figure 5, one can see that there was a pH effect. As the pH increased the amount of soluble silicon increased.

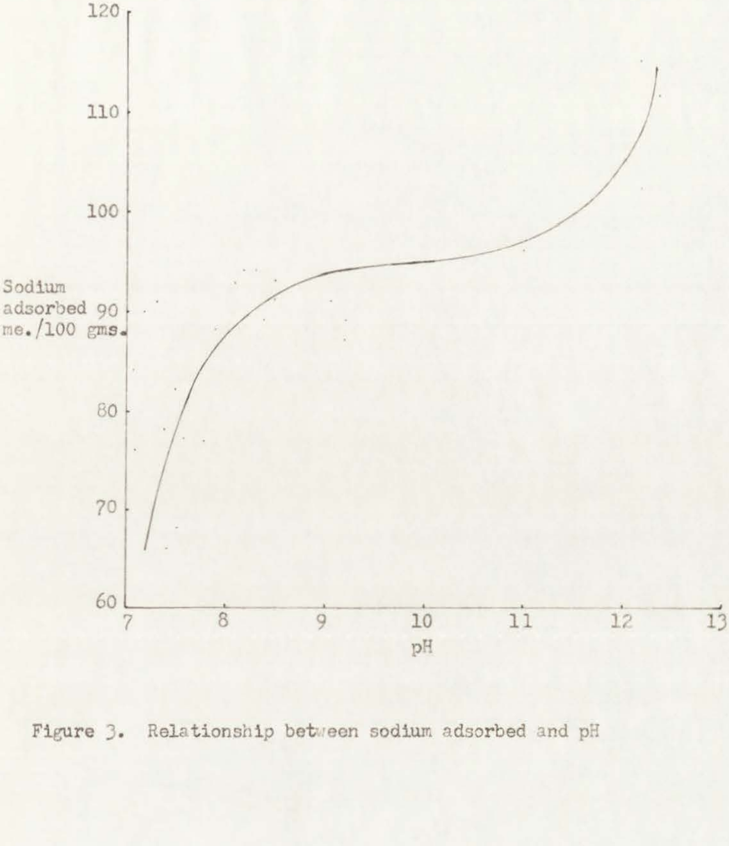

Figure 3. Relationship between sodium adsorbed and pH

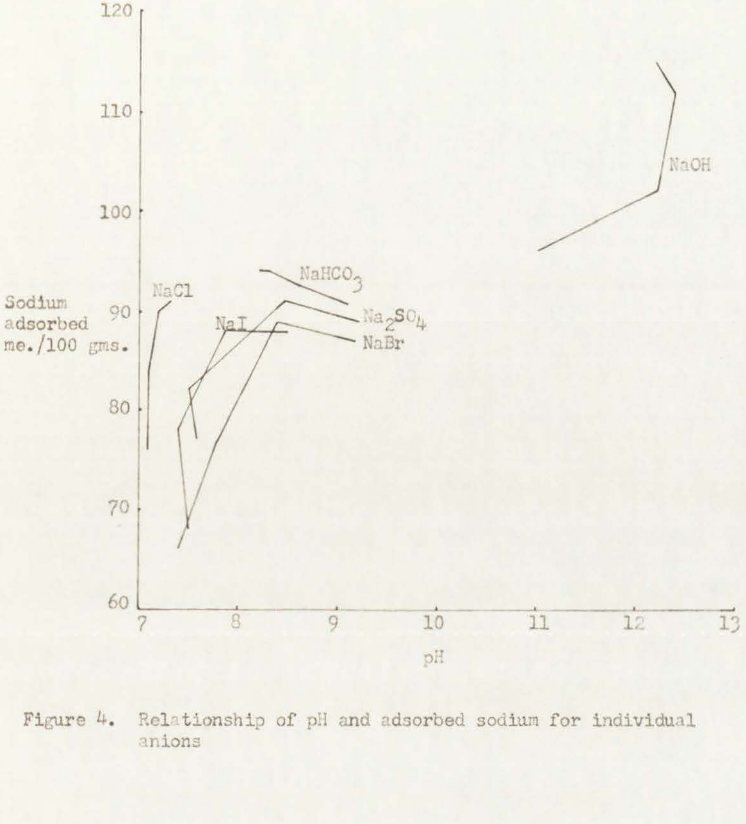

Figure 4. Relationship of pH and adsorbed sodium for individual anions

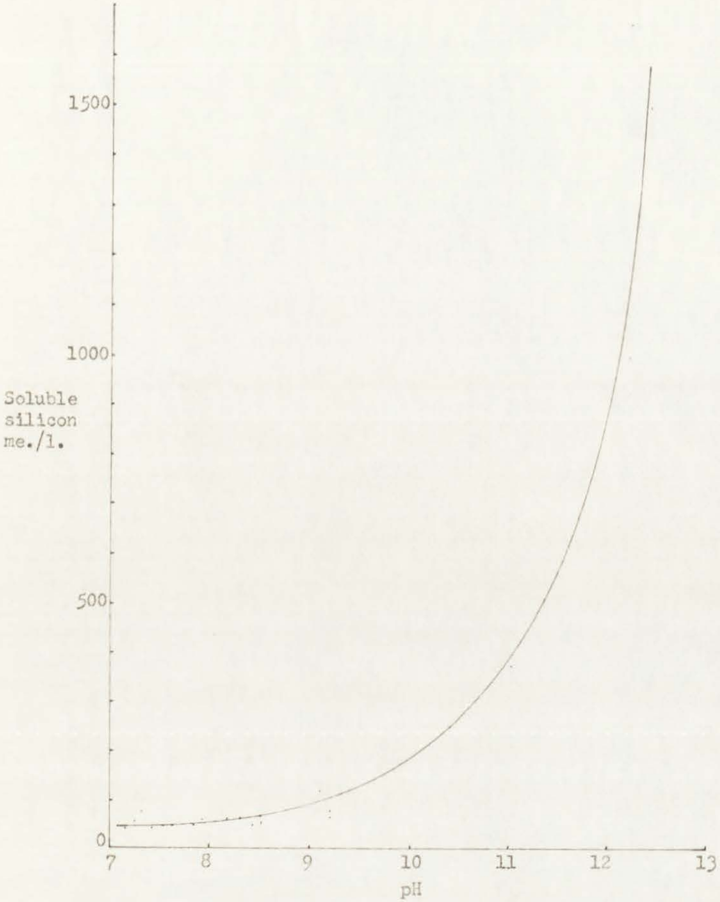

Figure 5. Relationship of pH and soluble silicon

The effect of pH in the systems for the different anions is shown in Figure 6. Under these conditions it is apparent that the anions in the system had an additional influence on the amount of soluble silicon. In the lower pH range the solubility of silicon, except in the chloride system, did not increase as rapidly with pH as it did in the higher range. Also, the effects varied with the ionic strength of the solutions. In the halide and sulfate systems the solubility increased with ionic strength as seen in Table 7, page 22. In the bicarbonate system there was a decrease in solubility of silicon when the ionic strength increased from 0.01 to 0.10, thereafter increased ionic strength had no effect. In the hydroxide system the solubility increased with ionic strength. The effects of the halides and sulfate appear to be similar in nature, as indicated by the shape of the curves in Figure 6, but the amount of soluble silicon varies with ionic strength as shown in Table 7.

The amount of soluble silicon in the equilibration extract was compared with the amount of sodium adsorbed, as shown in Figure 7. Careful examination of this curve shows that for the points lying to the left, a unit increase in soluble silicon resulted in a corresponding increase in adsorbed sodium as is shown in Figure 8. The relation between adsorbed sodium and soluble silicon for the hydroxide systems is: 1 milliequivalent of sodium was adsorbed per 100 grams of clay for each 68 milliequivalents per liter increase of soluble silicon as shown by the four points to the right in Figure 7. The relation for the bicarbonate was complex as is shown by the x's in Figure 7. It appears the effects of the halides and sulfate were similar in nature but different in magnitude, whereas the reactions of the bicarbonate

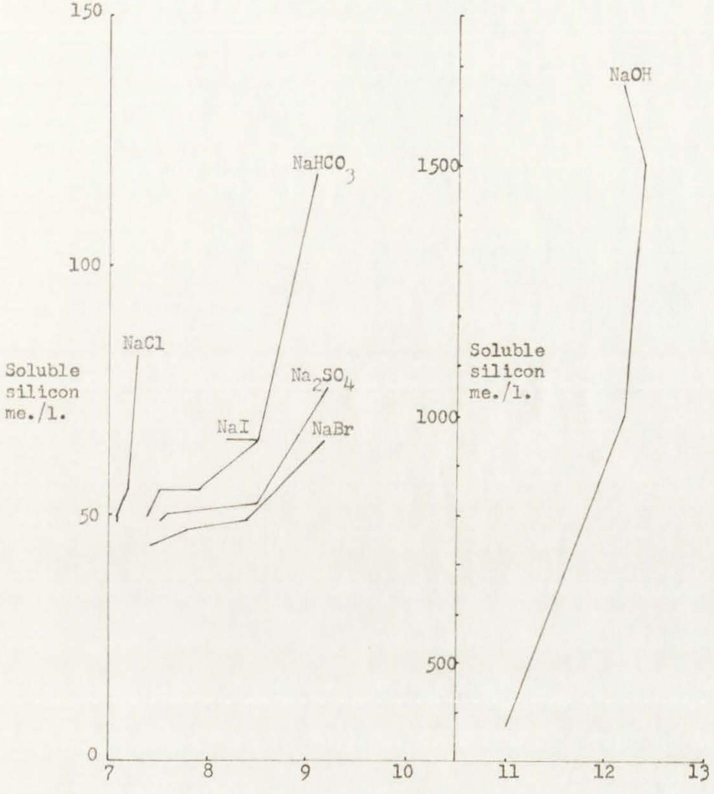

Figure 6. Relationship of pH and soluble silicon for individual anions

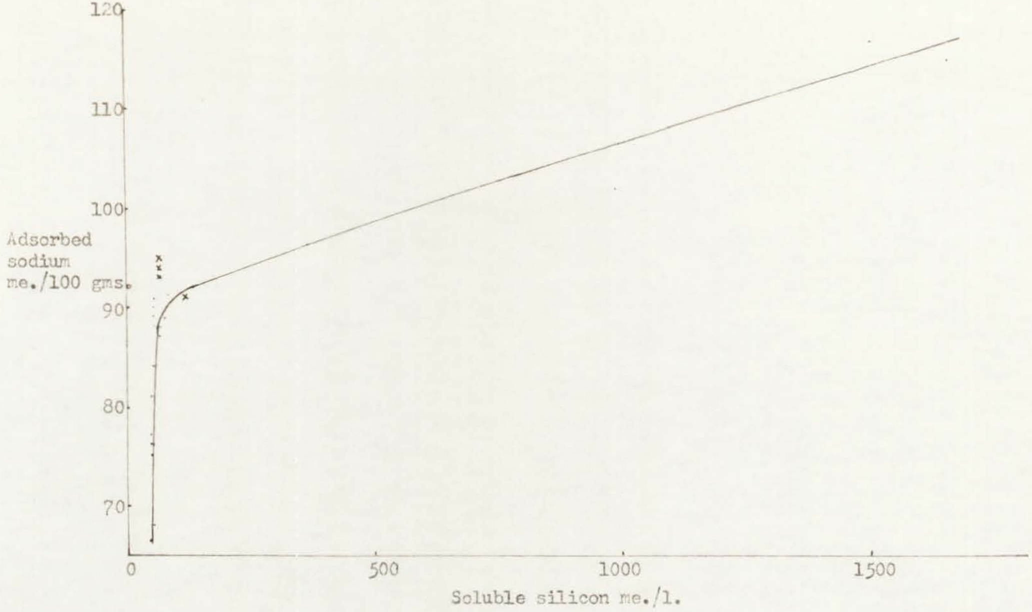

Figure 7. Relationship between soluble silicon and adsorbed sodium (x = bicarbonate ion)

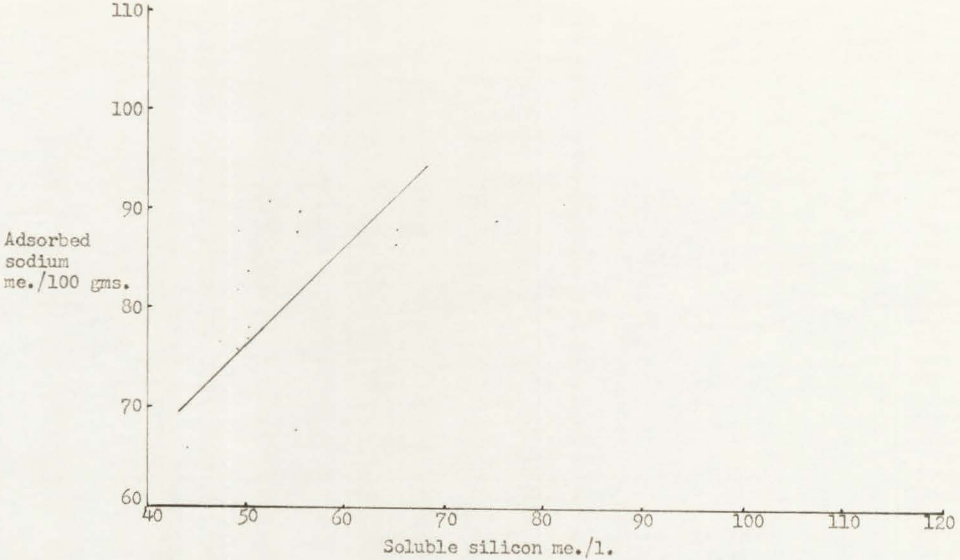

Figure 8. Relation between soluble silicon and adsorbed sodium for the halide and sulfate systems

and hydroxide ions were different in nature and magnitude.

From these evidences, it is apparent that the anions in the systems significantly influenced the amount of sodium adsorbed by the bentonite.

Generally, it has been accepted, that the electrophoretic mobility of a colloid and its capacity to adsorb cations are dependent upon charge density. Therefore the electrophoretic mobility and the adsorption capacity should be related. In as much as the capacity of the clay to adsorb cations is sensitive to the anions in the system, it is reasonable to assume the electrophoretic mobility of the clay would be affected in a similar manner.

With this reasoning, along with the limited data in Table 1, page 18, it appears evident that the anions in the systems affected the electrophoretic mobility of the clay in a similar manner as it did that of the capacity to adsorb sodium.

In the hydroxide, and to a lesser degree in the bicarbonate, system the clay appears to have undergone degeneration, as indicated by the amount of soluble silicon in the equilibration extract, shown in Table 7, page 22. There are three possible reactions which could account for the increased silicon in the extract. First, it is possible that silicate groups were released from corner and some edge positions of the crystal as a result of the formation of a more stable basic aluminum salt with the hydroxide ions in the system. In these positions, according to Grim (17), three of the oxygens in the tetrahedron would be shared by two adjacent silicon atoms in the silica layer and by an aluminum atom in the gibbsite layer. The fourth oxygen would be exposed and carry one negative charge. Loss of one of these silicate groups would therefore result in two ionized sites where only one existed previously. If this happens, then the number of ionized sites would increase directly with the number of silicate ions going into solution.

Second, some of the silica tetrahedrons may be replaced by $(OH)_4$ tetrahedrons, according to McConnell, as cited by Grim (17). This would increase the amount of soluble silicon in the system as well as increase the charge density of the clay.

Third, the clay may have undergone a more general degeneration. In which case the whole crystal would likely be affected. The alumina released would likely form basic salts as proposed by Henin (19). These basic salts could be formed with aluminum in combination with hydroxide ions and some silicate ions, but in lesser proportion than that found in the clay. The clay itself may form a basic salt with aluminum. Such degeneration would release silicon from the system as well as increase the charge density. It is quite possible that all of these reactions had a role in producing the results.

Further investigations would be desirable to answer the following questions. Do the relations, as observed in this study, apply to all clay minerals and for different cations in the system? Is the net effect the sum of the individual effects of all the anions in the system? What happens at the clay surface in the different environments? Answers to such questions would provide a better understanding of clays and their behavior.

SUMMARY AND CONCLUSIONS

Sodium saturated Utah bentonite was used in a study to determine the effects of various kinds of anions and ionic strength of the solutions on the sodium adsorption and electrophoretic mobility of the colloid. This clay, freed of all exchangeable calcium, magnesium, potassium, iron and aluminum was equilibrated with solutions containing various concentrations of sodium chloride, bromide, iodide, sulfate, bicarbonate and hydroxide. Effects of pH were determined by equilibrating the clay in sodium halide and sulfate solutions at pH levels of 7.2 and 10.5. The equilibration solution was analysed before and after equilibration to determine the extent of ion removal from the solution phase. The pH of the solutions before and after equilibration was also determined. Changes in the amount of sodium adsorbed, as a result of equilibration in the various solutions, were determined by extraction with ammonium acetate. Soluble silicon in the equilibration and ammonium acetate extracts was also determined. Electrophoretic mobility of the clay was measured by the moving boundary method.

It was found that the clay was sensitive to its anion environment. The amount of sodium adsorption and electrophoretic mobility of the clay and soluble silicon in the extract varied with the anions present. The amount of adsorbed sodium on the stock clay material was 93 milliequivalents per 100 grams. After equilibration in solutions having ionic strength of 1.0, the amount of sodium adsorbed was 66, 68, 76, 77, 94 and 115 milliequivalents per 100 grams of clay when the anions were bromide, iodide, chloride, sulfate, bicarbonate and hydroxide respectively. The effects of the anions generally decreased with lower concentration. The amount of sodium adsorbed was affected by pH. The amount of soluble silicon in systems was also affected by pH. A close correlation existed between the amount of sodium adsorbed by the clay and the amount of soluble silicon in the equilibration extract, which increased with the amount of cations adsorbed. For the halide and sulfate systems the ratio of the increase of soluble silicon to adsorbed sodium was in the order of 1:1, whereas in the hydroxide systems the ratio was in the order of 68:1.

The electrophoretic mobility also appeared to vary with the kind of anions and the ionic strength of the solutions in the systems. It increased according to the effectiveness of the anions to increase the amount of sodium adsorbed, but it decreased with increased ionic strength.

The results seem to justify two conclusions. First, the amount of sodium adsorbed, the electrophoretic mobility of the clay and the amount of soluble silicon were affected by the kind of anions and the ionic strength of the solutions in the systems. Second, the amount of sodium adsorbed, electrophoretic mobility of the clay and soluble silicon in the systems increased with pH.

LITERATURE CITED

(1) Audubert, René. Application of the Debye-Hückel theory to disperse systems. Trans. Farad. Soc. 36:144-153. 1940.

(2) Babcock, K. L., Carlson, R. M., Schulz, R. K., and Overstreet, R. A study of the effect of irrigation water composition on soil properties. Hilgardia 29 (3):155-164. 1959.

(3) Binder-Barhava, N., and Ravikovitch, S. Adsorption of sodium by soils from solutions of sodium salts. Soils and fertilizers 16:422. Abstract no. 2077. 1952.

(4) Bolt, G. H. Determination of the charge density of silica sols. Jour. Phys. Chem. 61:1166-1169. 1957.

(5) Bolt, G. H., and Miller, R. D. Calculation of total and component potentials of water in soil. Trans. Amer. Geophys. Union 39:917-928. 1958.

(6) Bower, C. A., Reitemeier, R. F., and Fireman, M. Exchangeable cation analysis of saline and alkali soils. Soil Sci. 73:251-261. 1952.

(7) Bower, C. A., and Truog, E. Base exchange capacity determination as influenced by nature of cation employed and formation of basic exchange salts. Soil Sci. Soc. Amer. Proc. 5:86-89. 1940.

(8) Christensen, Paul D., and Lyerly, Paul J. Water quality, as it influences irrigation. Texas Agric. Expt. Sta. Circular 132. 1952.

(9) Derjaguin, B. On the repulsive forces between colloid particles and on the theory of slow coagulation and stability of lyophobe sols. Trans. Farad. Soc. 36:203-215. 1940.

(10) Eaton, Frank M. Significance of carbonates in irrigation water. Soil Sci. 69:123-134. 1950.

(11) Fine, L. O., Williamson, E. J., Wiersma, Frank, and Umback, C. R. A study of the sodium adsorption ratio and residual sodium carbonate concepts of irrigation waters as they affect exchangeable sodium of soil under semiarid conditions. Soil Sci. Soc. Amer. Proc. 23:263-266. 1959.

(12) Glasstone, Samuel. An introduction to electrochemistry. New York: D. Van Nostrand Co., Inc., p. 533. 1942.

(13) Glasstone, Samuel. Thermodynamics for chemists. New York: D. Van Nostrand Co., Inc., p. 402. 1947.

(14) Greaves, J. C., and Linnett, J. W. Recombination of atoms at surfaces: part 6--recombination of oxygen atoms on silica from 20° C. to 600° C. Trans. Farad. Soc. 55:1355-1361. 1959.

(15) Greenberg, S. A. The depolymerization of silica in sodium hydroxide solutions. Jour. Phys. Chem. 61:960-965. 1957.

(16) Greenberg, S. A., and Price, E. W. The solubility of silica in solutions of electrolytes. Jour. Phys. Chem. 61:1539-1541. 1957.

(17) Grim, Ralph E. Clay mineralogy. New York: McGraw-Hill Book Co., Inc., pp. 56, 63. 1953.

(18) Harned, H. S., and Owen, B. B. The physical chemistry of electrolytic solutions. 3rd ed. New York: Reinhold Publishing Corp., pp. 553, 728-731. 1958.

(19) Henin, S. Synthesis of clay minerals at low temperatures. Clays and clay minerals. Proc. 4th Natl. Conf. on Clay Minerals Pub. 456, Natl. Acad. Sci., Natl. Res. Coun., Washington, D. C., pp. 54-56. 1956.

(20) Heston, W. M., Jr., Iler, R. K., and Sears, G. W., Jr. The adsorption of hydroxyl ions from aqueous solutions on the surface of amorphous silica. Jour. Phys. Chem. 64:147-150. 1960.

(21) Jackson, M. L. Soil chemical analysis. Englewood Cliffs, N. J.: Prentice Hall Inc., pp. 294-297. 1958.

(22) Joseph, A. F., and Oakley, H. B. The anomalous flocculation of clay. Nature 117:624. 1926.

(23) Kelley, W. P. Alkali soils. New York: Reinhold Publishing Corp., pp. 25-27, 145. 1951.

(24) Kelley, W. P. Adsorbed Na, cation exchange capacity and percentage Na saturation of alkali soils. Soil Sci. 84:473-478. 1957.

(25) Kelley, W. P., Brown, S. M., and Liebig, G. F., Jr. Chemical effects of saline irrigation water on soils. Soil Sci. 49:95-107. 1940.

(26) Lewis, G. C., and Juve, R. L. Some effects of irrigation water quality on soil characteristics. Soil Sci. 81:125-137. 1956.

(27) Longenecker, D. E., and Lyerly, P. J. Chemical characteristics of soils of west Texas as affected by irrigation water quality. Soil Sci. 87:207-216. 1959.

(28) Marshall, C. Edmund. The colloid chemistry of silicate minerals. New York: Academic Press Inc., 1949.

(29) Mattson, Sante. The laws of colloidal behavior I. Soil Sci. 28:179-220. 1929.

(30) McDonald, Robert S. Surface functionality of amorphous silica by infrared spectroscopy. Jour. Phys. Chem. 62:1168-1178. 1958.

(31) Nutting, P. G. The action of some aqueous solutions on clays of the montmorillonite group. U. S. Geol. Survey, Prof. Paper 197F:219-235. 1943.

(32) Oakley, H. B. The anomalous flocculation of clay. Nature 118:661-662. 1926.

(33) Overbeek, J. Th. G. Electrochemistry of the double layer. Colloid science, vol. 1, irreversible systems. Edited by H. R. Kruyt. Amsterdam: Elsevier Publishing Co., pp. 185, 309, 312-313. 1952.

(34) Ramdas, L. A., and Mallik, A. K. The effect of sodium chloride in improving the permeability of alkali soils. Curr. Sci. 16: 172-173. 1947.

(35) Schofield, R. K. Effect of pH on electric charges carried by clay particles. Jour. of Soil Sci. 1:1-8. 1949-50.

(36) Schofield, R. K., and Samson, H. R. The deflocculation of kaolinite suspensions and the accompanying change-over from positive to negative chloride adsorption. Clay Min. Bull. 2: 45-50. 1953.

(37) Sears, George W., Jr. Determination of specific surface area of colloidal silica by titration with sodium hydroxide. Anal. Chem. 28:1981-1983. 1956.

(38) Težak, Božo, Matijević, E., Schulz, K. F., Kratohvil, J., Mirnik, M., and Vouk, V. B. Coagulation as a controlling process of the transition from homogeneous to heterogeneous electrolytic systems. Disc. Faraday Soc. 18:63-73. 1954.

(39) Thorne, J. P., and Thorne, D. W. Irrigation waters of Utah. Utah Ag. Expt. Sta. and U. S. Soil Cons. Serv. Bull. 346. June, 1951.

(40) U. S. Salinity Laboratory Staff. Diagnosis and improvement of saline and alkali soils. Handbook 60, U. S. D. A., 1954.

(41) Verwey, E. J. W., and Overbeek, J. Th. G. Theory of the stability of lyophobic colloids. New York-Amsterdam-London: Elsevier Publishing Co., Inc., 1948.

(42) Wilcox, L. V., Blair, George Y., and Bower, C. A. Effect of bicarbonate on suitability of water for irrigation. Soil Sci. 77:259-266. 1954.

(43) Wiklander, Lambert. Cation and anion exchange phenomena. Chemistry of the soil. Edited by Bear, Firman E. New York: Reinhold Publishing Corp., p. 133. 1955.